

THERMAL DECOMPOSITION OF 1,2-DICHLOROBENZENE

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ABSTRACT

Incineration is emerging as the best long term solution to the management of hazardous waste. One problem of incineration is that compounds surviving the combustion process are emitted from the combustion chamber and can be emitted to the environment. Much of the public opposition to incineration is based on the fear that the combustion process will produce a more toxic by-product than the original wastes. To study this problem, tests were conducted in a laboratory scale test system that allows the establishment of a steady state combustion environment. The tests were run with 1,2-dichlorobenzene while varying the temperatures of the reaction zone, the residence time, and the oxygen concentration. The various tests produced different product distributions. The tests with excess oxygen and a moderate temperature of 750°C produced a small number of compounds at trace levels. Tests using 1,2-dichlorobenzene that were low in oxygen concentration produced as many as thirty compounds. The organic compounds identified from the thermal decomposition of 1,2-dichlorobenzene were unsaturated chlorinated aliphatic hydrocarbons, chlorinated cyclopentadienes, chlorinated benzenes, chlorinated phenols, chlorinated naphthalenes, and chlorinated benzoic acids.

INTRODUCTION

Modern society depends upon chemicals in nearly every aspect of life. This dependence is not available to us without costs. Every time a chemical is manufactured, it produces a waste stream at one step or another. In the past, these wastes have been dumped without regard to their effect on the environment. The first approach used to solve this problem was burial of the wastes. This has proven to be a tenuous solution at best with cases being reported every day where organic chemicals are reaching the ground water supplies. A more permanent solution to this problem is the incineration of these organic hazardous chemicals to produce water, carbon dioxide, and acid gases.

Incineration is not without its problems as well. Compounds containing halogens, sulfur, and nitrogen produce acid gases when combusted. These acid gases must be removed from the combustion

gas stream before they are emitted to the environment. Principal Organic Hazardous Constituents (POHCs) that survive the combustion process can still be emitted to the environment. Other compounds can be formed during the combustion process which are called products of incomplete combustion (PICs). These compounds could be more toxic than the original compounds being disposed of. Concern over the later two types of compounds led to the need for this research.

Dichlorobenzene (DCB) is a typical industrial organic compound. It is used in the manufacture of consumer products and as an intermediate for the production of dyes. Therefore, it was proposed to study the thermal decomposition of dichlorobenzene as a model compound to determine the extent of the production of products of incomplete combustion and under what conditions these products are produced.

Emission of PICs from Combustion Process

The evaluation of the POHC emission from hazardous waste incinerators has created an awareness of the total emissions from these combustion processes. Researchers who have tried to determine the identity and concentration of all of the organic compounds emitted during combustion have met with limited success. The possibilities of the compounds which can be formed are nearly endless. These studies have resulted in the identification of certain PICs that are of greatest environmental concern and have been listed as hazardous compounds in CFR 40, Part 261, Appendix VIII.¹ Some of the other more common compounds not listed in Appendix VIII have also been identified in these emissions.

Trenholm and Lee have evaluated the total mass emissions from several combustion processes. Their study evaluated nine industrial boilers that co-fired hazardous wastes, eight hazardous waste incinerators, five mineral processing kilns that fired hazardous wastes as a part of their fuel requirements and two municipal solid waste incinerators. They were able to identify 55 different compounds in the combustion gas stream from these units. About one-third of these compounds are listed in Appendix VIII.²

Wyss, Castaldini, and Murray published an EPA report on two different incineration sites and the PIC and POHC emissions produced. They reported that the PIC emissions were associated with high emissions of the POHCs. The ratio of the total PIC emissions to the total POHC emissions at the two sites were about 25 % and 80 %. The PICs identified were mainly chlorinated methanes, ethane, ethylenes, and propanes.³

Tiernan and co-workers sampled combustion gas streams from incinerators burning hazardous wastes for total mass emissions and found that the chlorophenols and chlorobenzenes were higher in concentration than the polychlorodibenzofurans (PCDFs),

polychlorodibenzo-p-dioxins (PCDDs), and the polychlorobiphenyls (PCBs). The PCDFs, PCDDs, and PCBs were present at only trace quantities. The tetrachloro dibenzo-p-dioxins were carefully examined for 2,3,7,8-TCDD and found it to be present at only a small percentage of the other TCDDs.⁴

Recent studies by the research group at the University of Dayton have shown a correlation of the ranking of organic compounds by thermal stability in low oxygen conditions with the destruction and removal efficiencies (DREs) observed in actual field studies.⁵ This group of researchers has also tested mixtures of six different compounds for thermal stability. They found that the relative thermal stability of compounds can change when they are present in mixtures as compared to testing the compounds alone.⁶ The six compounds carbon tetrachloride, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloroethylene, and toluene were present in the mixture. From the thermal treatment of these compounds, they were able to identify 58 different PICs. This testing was done in different atmospheres and at different temperatures. Not all 58 compounds were present in any of the individual tests. The PICs ranged from benzene to several polynuclear aromatic compounds and from chloroform to chlorinated benzenes and naphthalenes.

EXPERIMENTAL

Test Apparatus

The test combustion system has a sample introduction system, a preheater section, the high temperature reaction section, and the absorber section. The sample introduction system is composed of a pump, gas flow meters, and a spray nozzle. The pump delivers the test compounds to the introduction system at a set rate that can be adjusted to the desired level. The pump consists of a stainless steel reservoir that is pressurized with nitrogen. The outlet of the vessel is a fine metering valve that controls the flow of chemicals to the system. The gas flow meters are two sets of gas proportioning valves that allow for adjusting flows of up to three different gases in any proportion that is necessary to achieve the desired atmosphere for testing. The spray nozzle is used to atomize the test compounds into the preheater section. This is used to help evaporate the compounds and insure that the compounds are in the gas phase before entering the reaction zone. The preheater and reaction sections are tubes packed with an aluminosilicate fire brick material. The reaction tube has a section of coiled tube following the packed bed section. Tubes with two different lengths of coiled tube allowed the residence time of the system to be varied without changing the velocity through the system. The temperatures of the two heated zones can be controlled separately. The absorber section is a series of impingers containing solvents to condense and absorb organic compounds as they exit the heated zones.

Analysis Methods

The solvent used in the absorber section for these tests was methanol. Methanol would allow water and organic compounds to be dissolved in the solvent. The absorbing solutions were analyzed directly using GC/MS to determine the concentration of those compounds present at higher concentrations. The solutions from the first impinger were also concentrated by extraction into methylene chloride. The methylene chloride was then evaporated to a small volume and analyzed by GC/MS.

RESULTS

The decomposition system used in this research allowed the temperature, oxygen concentration, and residence time to be varied. These parameters were determined to have the highest probability of affecting the production of PICs and the survival of POHCs in the feed. These parameters were varied in an effort to determine the formation chemistry of the PICs.

The variation of the oxygen concentration had the most dramatic effect on the distribution of products. The tests where there was a calculated excess of oxygen in the system resulted in very few compounds being formed at temperatures of 750°C or higher. An intermediate number of compounds were formed in tests using a stoichiometric concentration of oxygen. In those tests where the oxygen concentration was at a substoichiometric concentration, there was a large number of compounds formed. Table I lists the compounds that were formed or that remained after combustion as a function of the oxygen concentrations. These three tests were performed under identical conditions on the same day with only the oxygen concentration being varied. The temperature of the tests was 750°C with about 2 seconds residence time in the system. The gas flow rate through the system was maintained at the same rate by the addition of more nitrogen to the system to make up for the decrease in oxygen flow in the system.

The variation of the temperature also produced a dramatic effect in the number of compounds being produced. Figure 1 shows the total ion chromatogram for a concentrated sample that was run at 700°C with a residence time of about one second. Figure 2 shows a sample that was run at 800°C with a residence time of about 2 seconds. Both samples were from tests that had an excess oxygen concentration. Figure 3 also illustrates the effect of temperature on the amount of DCB surviving the combustion process as a function of temperature and of oxygen concentration. At a temperature of 700°C, a relatively high concentration of DCB remained even with excess oxygen present. Increasing the temperature to 800°C lowered the concentration of DCB remaining by nearly two orders of magnitude even with a substoichiometric oxygen concentration.

The variation of the residence time had the smallest effect on the product distribution of the parameters studied. There was a slight enhancement of the amount of more highly chlorinated compounds formed as illustrated in Table II. Table II lists the relative amounts of PICs formed and the amount of DCB remaining for two tests that varied only in the length of time the compounds remained in the high temperature section of the system. The residence time in the high temperature region was varied by using two tubes with different lengths of post packed bed tube coils. This allows the residence time to be varied without altering the gas velocity in the packed bed section.

CONCLUSION

These studies have shown that factors such as temperature, oxygen concentration, and residence time can have an affect on the product distribution from a combustion reaction. In cases where moderate temperatures and excess oxygen are available, there is generally low levels of PICs formed as well as low concentrations of POHCs surviving the combustion reaction.

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Table I
EFFECT OF OXYGEN CONCENTRATION ON PRODUCT DISTRIBUTION

<u>Compound Present</u>	<u>Oxygen Concentration in Test</u>		
	<u>Excess</u>	<u>Stoic.</u>	<u>Substoic.</u>
Chlorobenzene	X	X	X
Dichlorobenzene	X	X	X
Trichlorobenzene	X	X	X
Tetrachlorobenzene	X	X	X
Pentachlorobenzene	X		
Hexachlorobenzene	X		
Chlorophenol			
Dichlorophenol		X	X
Trichlorophenol		X	X
Tetrachlorophenol		X	X
Pentachlorophenol		X	X
C ₄ H ₆ Cl ₂	X		
C ₅ H ₁₀ Cl ₂	X		
C ₅ H ₁₀ OCl	X		
Hexachlorobutadiene	X		
Dichlorobutetetraene			X
Propanedioic acid, Dimethyl ester			X
1-Chloro-4-ethynyl-Benzene		X	X
Methyl Benzoate			X
Tetrachlorobutene			X
C ₈ H ₄ Cl ₂		X	
Chlorobenzofuran		X	X
Dichloro-(chloromethyl)-benzene		X	
Naphthalene			X
C ₈ H ₆ Cl ₂			X
Chlorobenzoic Acid methyl ester		X	X
Chloronaphthalene			X
Dichlorobenzofuran		X	X
C ₈ H ₇ Cl			X
Dichlorobenzoic acid methyl ester		X	X
Acenaphthalene			X
C ₁₀ H ₈ Cl ₂		X	X
Dichloronaphthalene		X	X
C ₁₂ H ₇ Cl			X
C ₁₀ H ₇ Cl ₃			X
Chlorodibenzofuran			X
Trichloronaphthalene		X	X
Tetrachlorobenzofuran			X
Dichlorodibenzofuran		X	X
Tetrachloronaphthalene		X	X
Trichloro-diphenyl ether			X
Trichloro-1,1'-Biphenyl		X	X
Trichlorodibenzofuran			X
Tetrachloro-1,1'-Biphenyl		X	X
Tetrachlorodibenzofuran		X	X
Dichloronaphthol			X
Tetrachloronaphthol			X

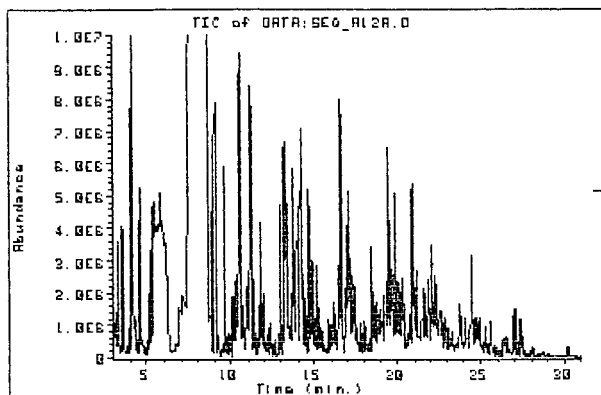


Figure 1. Chromatogram of Concentrated Sample ran at 700°C, 1 second residence time.

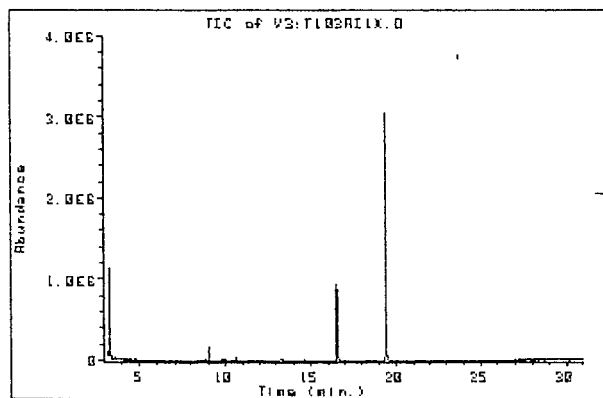


Figure 2. Chromatogram of Concentrated Sample ran at 800°C, 2 second residence time.

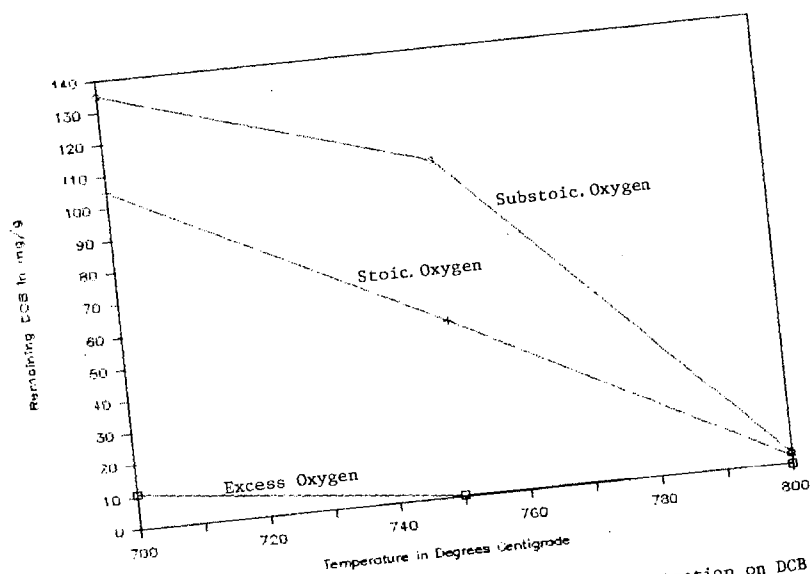


Figure 3. Effect of temperature and oxygen concentration on DCB surmising combustion.

Table II
EFFECT OF RESIDENCE TIME ON PRODUCT DISTRIBUTION

Compounds Present	Amount/g of Parent Material	
	1 Second	2 Second
Chlorobenzene	7.5 ug/g	17.7 ug/g
Dichlorobenzene	62 ug/g	372 ug/g
Trichlorobenzene	173 ug/g	0.78 ug/g
Tetrachlorobenzene	113 ug/g	0.30 ug/g
Pentachlorobenzene	79 ug/g	1.42 ug/g
Hexachlorobenzene	32 ug/g	7.48 ug/g

**Effects of Pretreatment Conditions on the Activity of a Pt/Al₂O₃
Catalyst for the Oxidation of Di(n-)propyl Sulfide**

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Introduction:

Organic sulfur compounds are known to poison noble metal catalysts and are often present in stream of air which must be purified. Sulfur compounds may poison platinum oxidation catalysts by adsorbing onto active sites. When the concentration of the organic sulfur compound is high enough to saturate the catalyst surface, oxidation of the more reactive organic molecules will not occur until temperatures sufficient to destroy the sulfur compounds are reached (1,2,3). Because of this, it is important to gain an understanding of the behavior of different chemical states of supported platinum when exposed to known catalytic poisons.

The temperature at which a Pt/Al₂O₃ catalyst is calcined in air has been shown to influence both the dispersion and chemical state of platinum (4-11). Platinum dispersion increases following air calcination up to 550-600°C. Calcination above this temperature has been shown to severely decrease dispersion (5,6,8,11). Pt/Al₂O₃ catalyst, prepared from H₂PtCl₆ will form platinum(IV) complexes when calcined between 300-600°C, while metallic platinum crystallites are formed following calcination at higher temperatures (5-7). Platinum is reported to be more active as a metal, onto which oxygen is chemisorbed, for oxidation reactions involving organics (1,7,12). Volter et al. (7) studied the n-heptane oxidation activity of these complexes between 150 and 300°C. The activity of the catalyst (prepared from H₂PtCl₆) was shown to increase with an increase in calcination temperature (between 500°C and 900°C). From this work they concluded that reduced platinum is more reactive than oxidized platinum for complete oxidation of n-heptane.

This work investigates the activity and poison resistance of a supported platinum catalyst as a function of the catalyst oxidation state resulting from different pretreatments.

Experimental:

Materials: The Pt/ γ -Al₂O₃ catalyst used in this study was obtained from Houdry. It contained 1% platinum by weight and was prepared from H₂PtCl₆. The nominal BET surface area is reported to be 200 m²/g.

Apparatus: Reaction studies were performed using a fixed-bed reactor. Pre-purified air was further purified by passing through a drierite/13X filter in order to remove any traces of water. Air flow to the reactor was controlled by a 0-2.0 Nl/min (Nl defined as a liter at 0°C, 1 atmosphere) mass flow controller. Di(n)-propyl sulfide was injected into the air stream using a syringe pump. This produced a near constant concentration of 100 ppm (v/v) di(n)-propyl sulfide in air stream. The reactor consisted of a 0.75 cm id 316 stainless steel tube, approximately 5 cm in length. Three type K thermocouples were evenly distributed along the reactor and extended into the catalyst bed. A preheater was located just above the catalyst bed. Both the reactor and preheater were surrounded by an aluminum block which served as the furnace. Reactor temperature was controlled to $\pm 0.5^{\circ}\text{C}$ by controlling the temperature of the block. The temperature differential along the catalyst bed did not exceed 2°C during any of the runs. The concentration of sulfur containing compounds present in the reactor effluent was analyzed using a Hewlett-Packard 5790 GC equipped with a flame photometric detector (FPD) and modified for automatic sampling.

Procedure: Approximately 0.145g of 35-65 mesh (U.S. series) catalyst particles were diluted with crushed glass of a similar size so as to achieve a bed volume of 2 cm^3 . The catalyst was pretreated by first drying for 4 h at 125°C in pretreatment gas (air or 8% H_2 in He), after which, the catalyst bed was raised to the pretreatment temperature at approximately $4^{\circ}\text{C}/\text{min}$. Pretreatment temperatures of 300°C , 410°C , 600°C and 800°C were employed using a gas flow rate of 1.0 Nl/min. The final pretreatment temperature was maintained for 16 hours. At pretreatment temperatures of 410°C and below, pretreatment was carried out *in-situ*. When employing higher temperatures, the catalyst was placed inside a quartz tube furnace and heated to the desired temperature, which was maintained for 16 h. The catalyst was then cooled in flowing helium, weighed, diluted with glass and introduced to the reactor.

Following pretreatment, the reactor was adjusted to 230°C , which was the temperature employed for all runs. The reactor was sealed and di(n)-propyl sulfide flow was established (100 ppm in 1.7 Nl/min air) through the reactor by-pass. When the concentration of sulfide remained constant (about 2 hours), feed gas was diverted to the reactor. All lines were heated electrically at $125\text{-}150^{\circ}\text{C}$ in order to avoid condensation. Conversions were determined as a function of time-on-stream from the concentration of di(n)-propyl sulfide in the effluent stream. A blank run was performed prior to reaction studies. This run indicated that the reactor walls and glass diluent were inert at reaction conditions.

XPS Analysis: XPS spectra of fresh and spent catalyst were recorded using a Perkin-Elmer Phi 570 ESCA/SAM system employing $\text{MgK-}\alpha$ x-rays. The system was equipped with a reaction chamber which allowed for recording spectra of catalyst following pretreatment at temperatures below 550°C without exposure to atmosphere. Materials which were calcined at higher temperatures were analyzed following pretreatment in a quartz tube furnace. Spent catalyst were analyzed following removal from the reactor and separation from the glass diluent. Platinum

spectra were recorded following 100 to 200 scans of the 4d photoelectron region so as to reduce signal-to-noise. No shifting of peaks were observed during the scanning process indicating that the prolonged exposure of the sample to the x-ray source did not alter the platinum oxidation state. All binding energies are referenced to the aluminum 2p photoelectron peak at 74.0 eV. This was used as a reference since the position of this peak is invariant to the pretreatments employed here (4).

Results and Discussion:

Figure 1 shows the platinum 4d photoelectron region of the catalyst following calcination at temperatures of 300°C, 410°C, 600°C and 800°C (spectra A through D, respectively) and exposure to hydrogen at 300°C (spectrum E). The platinum 4f region, which exhibits the strongest signal, could not be analyzed due to interference with the aluminum 2p photoelectron peak. The binding energy of the 4d_{5/2} photoelectron peak for the catalyst calcined at 300°C and 410°C is 317.0±0.2 eV. This binding energy is consistent with studies performed elsewhere (4,13) and indicates platinum is in an oxidized environment. As the calcination temperature is increased from 410°C to 600°C, a strong shoulder at approximately 315.0 eV becomes evident. Further increasing the calcination temperature to 800°C results in a decrease of 2.0 eV in the binding energy of the platinum 4d_{5/2} photoelectron peak. Similar changes in binding energies have been reported (4,13,14) and are indicative of reduced supported platinum. It is clear from this figure that increasing the calcination temperature from 410°C to 800°C results in increasing the extent of platinum reduction. The majority of the platinum is in the oxidized state following calcination at 300°C and 410°C, while the majority of the platinum is in a reduced state following calcination at 800°C. These results are consistent with those of Lieske and co-workers (5-7), who have extensively studied platinum species formed following calcination of Pt/γ-Al₂O₃ catalysts prepared from H₂PtCl₆. Their results showed that calcination below 600°C yields platinum(IV) species, while calcination at higher temperatures leads to the formation of metallic platinum.

Figure 2 illustrates conversion as a function of time on stream for catalysts pretreated at different calcination temperatures. No partial oxidation products were detected. Sulfur balances were performed on the effluent during all runs and were between 85 and 96% for the period of 3 hours into the run until the run was terminated. Discrepancies in the sulfur balances were attributed to formation of SO₃, which could not be analyzed. Calcination at 300°C yields a catalyst which deactivates throughout the duration of the run. Increasing the calcination temperature to 410°C improves the catalyst performance. Following an initial rapid deactivation, the catalytic activity increases, achieving an ultimate conversion of 71%. Increases in activity of oxidation catalysts during start-up have been reported elsewhere (15). The cause of the initial sharp decrease in activity was not investigated. However, complexing of surface platinum with adsorbed sulfur or the presence of chlorine on the sample may be responsible for this behavior. Further increasing the calcination temperature to 600°C decreases the catalytic activity (relative to the sample calcined at 410°C). In this instance, the steady-state conversion was 40%. A further decrease in activity is observed upon increasing the

calcination temperature to 800°C.

Following an initial induction period, catalysts calcined at 410 and 600°C increased to a stable level of activity. However, the catalyst calcined at 300°C continued to deactivate throughout the duration of the run. Lieske and co-workers (5,6) have demonstrated that calcination at 300°C will yield a different oxidized platinum species than that produced following calcination at higher temperatures. Apparently, this species is somewhat susceptible to deactivation in the presence of sulfur compounds.

Figure 3 compares the activity of the catalyst calcined at 800°C to that of the catalyst reduced in hydrogen at 300°C. Catalysts were analyzed following the run by XPS. Results indicated that the reduced platinum was not oxidized during the reaction exposure. In both cases, a rapid loss of activity was followed by a steady, low level of conversion. Pretreatment in hydrogen at low temperatures is reported to yield a highly dispersed reduced platinum phase (14), while calcination at high temperatures is reported to yield a poorly dispersed reduced platinum phase (5,6,8,11). Note that in spite of the expected difference in platinum dispersion, the two materials possess similar catalytic properties. This suggests that the loss of catalytic activity observed upon increasing the calcination temperature from 410°C to 800°C cannot be attributed solely to decreased platinum dispersion.

The activity of the Pt/Al₂O₃ catalyst studied here was found to be a strong function of the platinum oxidation state. As the extent of platinum reduction is increased, the catalytic activity for complete oxidation of di(n)-propyl sulfide decreases. Reduced platinum is believed to be more reactive than oxidized platinum for reactions involving complete oxidation of hydrocarbons (1,7,12). Volter et al. (7) has shown that while increasing the calcination temperature from 500°C to 900°C dispersion decreases, the activity of Pt/Al₂O₃ for oxidation of n-heptane increases. Although platinum dispersion will be altered by the different pretreatments, it is not felt that differences in catalytic activities observed here is the sole result of dispersion. Note that while the extent of reduction is similar for catalysts pretreated in hydrogen at 300°C and calcined at 800°C, a different dispersion is expected but the catalytic behavior is similar. This indicates that the oxidation state is an important consideration in determining the activity of supported platinum catalysts. Chlorine is known to poison platinum oxidation catalysts (1,10). No chlorine could be detected from catalysts calcined at 600°C and above, based on wet chemical analysis, yet these materials possessed the lowest level of activity. Because of this, it was not felt that chlorine played a major role in determining catalytic activity. The differences in reaction behavior, as illustrated in Figure 2, are attributed to the relative amounts of reduced and oxidized platinum species, with the oxidized species being more efficient in sulfide oxidation.

The presence of sulfur compounds in mixed feed streams has been shown to severely reduce hydrocarbon oxidation activity through adsorption onto the catalyst surface (2,3,16). It is possible that while the reduced metal phase is more active in hydrocarbon oxidation, it is much more susceptible to sulfur poisoning in that sulfur

will adsorb onto the metal and effectively block the active site. The oxidized platinum species, while not as active towards hydrocarbon oxidation (7), apparently is more resistant to sulfur poisoning and hence more active than the reduced platinum phase.

Conclusions:

Increasing the calcination temperature of a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst from 410°C to 800°C will result in decreased catalytic activity due to an increase in the extent of platinum reduction. The reduced metal phase is inferior in terms of activity and poison resistance to the oxidized metal phase in the complete oxidation of di(n-propyl sulfide).

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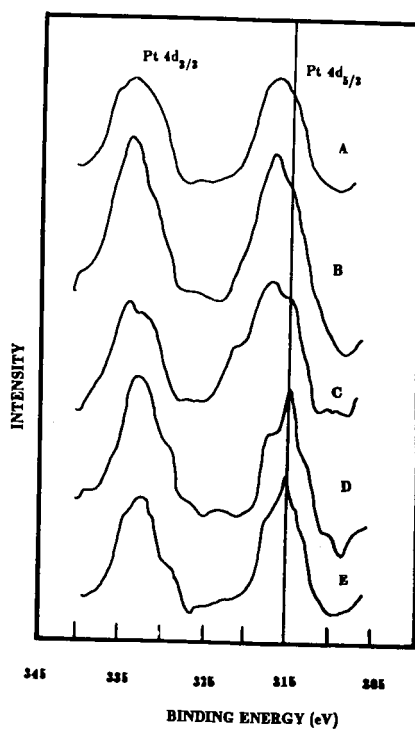


Figure 1: XPS spectra of the platinum 4d photoelectron region for a 1% Pt/Al₂O₃ catalyst following 16 hours calcination in flowing air and 16 hours reduction in hydrogen at 300°C. A) calcination at 300°C, B) calcination at 410°C, C) calcination at 600°C, D) calcination at 800°C and E) reduction in hydrogen at 300°C.

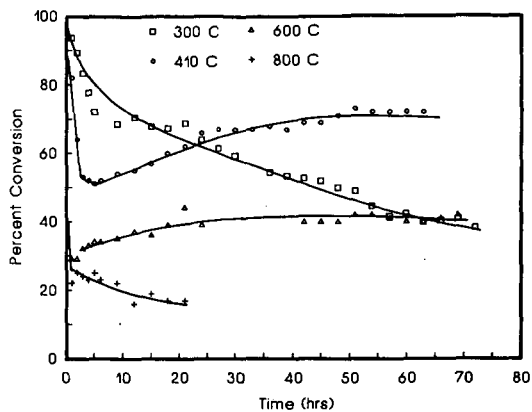


Figure 2: Conversion of di(n)-propyl sulfide (100 ppm in 1.70 Nl/min air) as a function of time on stream for catalysts calcined at different temperatures. ■ 300°C, ● 410°C, ▲ 600°C, + 800°C.

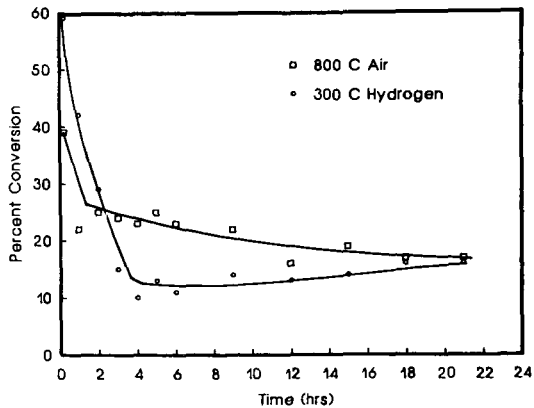


Figure 3: Conversion of di(n)-propyl sulfide (100 ppm in 1.70 Nl/min air) as a function of time on stream for catalysts pretreated in air at 800°C and in hydrogen at 300°C.

THERMAL BLACK FORMATION
DURING DESTRUCTION OF LIQUID WASTES
BY SUBMERGED ARCS

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ABSTRACT

Submerged, electrical arc discharges are an effective means for destruction and minimization of liquid wastes. Solutions of wastes, or waste liquids, are pyrolyzed by the arc to form gases, solid thermal blacks, and inorganic precipitates. This paper reports on an investigation of the thermal blacks produced by a specific submerged arc technology. With this process, multiple arcs are struck at the interface between an insulating organic oil phase and a conducting water phase. The high temperatures of the arc causes fast thermal pyrolysis of the adjacent organic material to occur in the presence of water vapor.

Three different organic phases were investigated; heptane, diesel fuel, and toluene. The thermal blacks produced by these different organic liquids were subjected to elemental analyses and found to be distinctly different in their ratio of carbon to hydrogen and carbon to oxygen. These differences may reflect the mechanisms by which the graphite structures form from the different types of organic feed stocks.

Introduction

The Al-Chem Detoxifier is a patented process being developed to treat liquid wastes. This technology creates an electrical arc discharge at a submerged oil-water interface. The high temperature of the electrical arc causes fast pyrolyses of the oil phase in the presence of water. Hence, the oil, water and any soluble waste organics dissolved in either phase are destroyed. A predominately hydrocarbon gas phases is produced and withdrawn from the unit. Inorganic precipitates and a suspension of solid thermal blacks also form. The thermal blacks are particularly troublesome, since they are electrically conductive and remain suspended in the organic phase. At some point during the operation, their concentration level becomes sufficient to cause a short of the high electrical potential needed to produce the arc discharge. At this point the unit fails to function. Hence the initial studies with the Al-Chem Detoxifier have been directed at the thermal-black formation process and potential methodologies for abatement.

Three different types of hydrocarbon liquids were used in the studies on thermal black formation. Heptane was selected to represent aliphatic liquids. Diesel fuel represented naphthenic structure and toluene the liquid aromatics. The heptane and

toluene were pure liquids compared to diesel and gasoline which are blends of hydrocarbons and have relative octane ratings and volatilities. However, they are also more typical of the organic solvents associated with waste liquids to be treated for disposal in later demonstrations.

EXPERIMENT APPROACH

The different organic liquids were charged to bench scale Al-Chem Detoxifier units. The operation and description of these units are described in other publications.

(1) (2) (3) (4). These small units were operated for periods of four to twelve hours. During this period, samples of the pyrolysis gases formed were collected for analyses.

After the run was completed, the thermal blacks which had been generated were filtered through a 10 micron filter, then dried. The dried thermal black was then subjected to elemental analyses and in some cases examined microscopically with ESM. The better ESM studies, however, were obtained by passing dilute suspensions of the organic liquid with its thermal black through 5 micron millipore filters, then subjecting the filter medium to ESM. The elemental analysis, gas analysis, and ESM work were all done at commercial laboratories on a fee basis.

DISCUSSION OF RESULTS: GASES

The composition of the gases formed during the pyrolysis process are shown in Table 1, except for toluene. Gases produced with this liquid hydrocarbon feed have yet to be analyzed. The gas compositions are shown primarily as a means of providing insights into the pyrolysis process and the subsequent formation of the thermal blacks.

Typical of any pyrolytic process for hydrocarbons which takes place at elevated temperatures, hydrogen and unsaturated hydrocarbons were produced in abundance. Since water was present in our process, carbon monoxide and dioxide were also formed. With the Al-Chem apparatus, the electric arc probably exceeds 2000°C. However, because the arc discharge zone is small relative to the bulk volume of the unit, the bulk temperature of surrounding liquids is limited to 70°C. This means that products of the pyrolysis reaction are quickly quenched and cannot reach a thermodynamic equilibrium at the arc temperature. Hence acetylene, which is unstable at 70°C based on thermodynamic considerations, remains an abundant species of the gases produced. However, with the aliphatic hydrocarbon liquids, it is the acetylene which is suspected as being a major source of the thermal blacks formed.

While the n-heptane and gasoline show similar trends in gas compositions, the gasoline produced significantly more of the heavier C₅ vapors. This was felt to be due to the lighter hydrocarbons added to the gasoline to increase volatility. At

70°C these light hydrocarbons were being stripped from the gasoline without being subjected to the pyrolytic action of the transfer arc. The diesel fuel, representative of naphthenic hydrocarbons gave a different distribution of product gases. These saturated ring structures produced more hydrogen and oxides of carbon than the aliphatic hydrocarbon liquids. In the case of the naphthenic hydrocarbons, therefore, it is postulated that the graphitic thermal blacks are generated by combination of modified ring structures already present in the liquid hydrocarbon feeds. Similar behavior appears to take place with the aromatic hydrocarbon feed stocks. The aliphatic liquid hydrocarbons, however, must form ring structures from unsaturated acetylenes or alkenes prior to thermal black formation..

SOLIDS

The information shown in Table 2 summarizes the various aspects of the thermal blacks formed. The diesel, representing the naphthenic liquid hydrocarbons, forms the greatest amount of thermal black per unit of power input. The data for toluene are missing, but it too is expected to show a rather significant production of thermal black for power input. The remainder of the table shows the chemical make up of the thermal blacks with respect to their carbon, hydrogen and oxygen contents. Although small amounts of nitrogen and ash appeared during the analyses of the thermal blacks, these were discarded in later calculations. Of the organic liquids which were run, the gasoline gave the greater variation. This was attributed again to the nature of gasolines as blends of various liquid hydrocarbons to produce the desired octane and volatility characteristics. A summary of these data indicate the following possible orders for the atomic ratios for the thermal blacks formed.

C/H Molar ratio	aromatic > aliphatic > naphthamics
C/O Molar ratio	aromatic > naphthenic > aliphatic

The carbon to hydrogen ratio speaks both to the type of feed stock organic used and to the mechanism by which the thermal blacks are formed. Aromatics have higher C/H ratio to begin with, and their unsaturated, stable rings can polymerize to the thermal black structure by hydrogen losses and free radical formation on the rings. The free radicals then terminate through combination mechanisms. Naphthenic feedstocks need not lose as much hydrogen to proceed through this polymerization process. Aliphatic materials must lose proportionately more hydrogen to become sufficiently unsaturated (acetylene) prior to formation of cyclic rings rather than linear or brached thermal blacks.

The carbon to oxygen ratio on the other hand speaks to the degree to which oxygen apparently takes part in ring structures and the termination of the free radicals. Oxygen is known to form both stable five membered (ether) rings with carbon and to suppress free radical polymerization processes. In either case the order shown in Table 2 was not unexpected.

Finally a potential chemical formula for high color channel black of a commercial variety is shown in Table 2.(5) This suggests that in comparison to commercial thermal blacks, those produced by the Al-Chem Detoxifier have approximately the same oxygen content but considerably more hydrogen. This may well reflect the nature of the submerged arc pyrolysis process in which free radicals are generated and then abide in the hydrogen rich medium of the liquid hydrocarbon where transfer processes represent a termination procedure.

SUMMARY

Thermal blacks produced by submerged electrical transfer arcs in the presence of water have chemical structures characteristic of the liquid hydrocarbon feedstocks from which they are produced. Although these thermal blacks have much the same physical characteristics as commercial thermal blacks, they are much richer in hydrogen content. This suggests that they are not quite the same polyaromatic or graphitic type structures as commercial thermal blacks.

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TABLE 1

GAS PHASE COMPOSITIONS FOR DIFFERENT FEEDSTOCKS

Feed Liquids

<u>Oil Phase</u>	<u>n-Heptane</u>	<u>Diesel</u>	<u>Gasoline</u>
<u>Water Phase</u>	<u>Tap Water</u>	<u>Tap Water</u>	<u>Tap Water*</u>
Component	Mole percent		
Hydrogen (H ₂)	56.4	63.9	41.8
Carbon Monoxide (CO)	12.7	17.0	11.3
Acetylene (C ₂ H ₂)	11.4	6.3	5.6
Ethylene (C ₂ H ₄)	7.9	2.3	2.7
Methane (CH ₄)	4.3	2.5	3.0
Pentene +(C ₅ =+)	3.0	3.5	18.0
Carbondioxide (CO ₂)	0.9	3.2	1.3
Propylene (C ₃ H ₆)	1.2	0.6	1.43
Misc. (Hydrocarbons)**	2.2	0.7	15.0

*Tap water contained 0.5M hydroquinone

**Predominatley unsaturated hydrocarbons

TABLE 2
CARBON BLACK ANALYSES FOR EXPERIMENTAL RUNDS

		Organic Hydrocarbon Phase			
		<u>Heptane</u>	<u>Gasoline</u>	<u>Diesel</u>	<u>Toluene</u>
Thermal Black Formation Rate (gram/kw hr)		12.53	3.64	41.38	--

Atomic Weight %	C	86.33%	85.76-92.15%	87.01-82.76%	93.59%
	H	3.23%	2.57-03.17%	7.61-10.82%	1.38%
	O	10.42%	11.66-04.67%	5.42-06.45%	5.03%

Possible Molecular Formula		C ₁₁ H ₅ O	C ₁₁ H ₄ O or C ₂₆ H ₁₁ O	C ₂₁ H ₂₂ O or C ₁₇ H ₂₇ O	C ₂₅ H ₄ O

C/H Molar Ratio		2.2	2.95-2.36	0.95-0.63	6.25
C/O Molar Ratio		11.0	11.0 -26	17 - 21	25

Commercial high -color channel blacks

Molecular Formula C₃₇H₂O₃ C/H = 18.5 C/O = 12.3